

Interactive comment on “Evidence for renoxification in the tropical marine boundary layer” by Chris Reed et al.

Anonymous Referee #1

Received and published: 31 January 2017

General comments:

The Authors present a compelling set of model results to explain the chemistry underpinning commonly observed daytime maxima in NO_x at the Cape Verde Atmospheric Observatory. The impact of condensed phase nitrate photolysis in improving understanding of the NO_x cycle in the marine boundary layer from long-term datasets, which capture diurnal features, has not been presented to date. This manuscript provides a robust method with which to test the findings of intensive field and lab observations of this phenomenon. The authors also find that the role of halogens is important in describing several features in the temporal nature of the NO_x diurnal patterns, building on recent findings that such chemistry may be important in controlling the cycling of reactive nitrogen in remote marine regions. The presented manuscript is well-written and most of the data in the figures is presented clearly. Overall, this work is acceptable

C1

for publication in Atmospheric Chemistry and Physics after a number of minor revisions and technical corrections have been made, which are presented in detail below.

Minor comments:

1) The title of the manuscript does not convey two of the major topics of this paper, nitrous acid and halogen hydroxides. The authors should consider modifying their title to reflect the important roles of HONO and halogens on renoxification processes in this work.

2) The authors cite a number of real-world surface (Baergen and Donaldson, 2013; Ye et al., 2016a), laboratory substrate studies (Handley et al., 2007; Scharko et al., 2014; Zhou et al., 2003), a model estimate (Cohan et al., 2008) and two works on aerosol nitrate catalytic degradation (Ndour et al., 2009) and photolysis (Ye et al., 2016b) as the basis for parameterizing the particulate nitrate conversion rates in their model (e.g. Pages 7-8). The majority of the cited work is for nitrate photolysis on proxy surfaces at the atmospheric interface and this is not clearly stated throughout the manuscript, which makes the focus on aerosol nitrate photolysis throughout the manuscript somewhat confusing. The connection and implications of linking nitrate photolysis on/in these other condensed phases is not clear in its applicability or in its limitations and this would be worth expanding on in the manuscript. This photochemistry is obviously important in this environment, but if studies of surface media and bulk aqueous solution (Scharko et al., 2014) are used to constrain the rates in the model and contribute to the discussion (e.g. effects of pH and RH), then the discussion should be expanded to include the expected role of surfaces versus aerosols in the MBL or how the parameterization of aerosol photolysis encompasses all of these sources.

3) The rapid photolysis of aerosol nitrate suggests that the lifetime of the reservoir may be quite short during the day (~hours, (Ye et al., 2016b)), but this may be dependent on the chosen photolysis rate. It would be worthwhile to discuss this and present the diurnal trend from the model (or indicate that this term is held constant) to compare to

C2

these previous findings. Clarifying whether the aerosol nitrate photolysis mechanism can operate on the ambient aerosol observed without depleting it and discussing how the reservoir is maintained would improve the argument that this is a reasonable HONO and NO_x source.

4) The (Crilley et al., 2016) manuscript only cites a (Heland et al., 2001) paper on the LOPAP, without any operational details on how such low detection limits were achieved for the instrument used in this work. The majority of the data in Figure 2 are below the stated LOD of the LOPAP (< 1 pptv), suggesting that this data has an associated high uncertainty, which is not depicted. What is the exact LOD of the instrument and what data can be reliably reported in this figure? It would also be helpful to present the methods for calibration, background correction, and determining the precision and accuracy of the measurements, as those achieved here are non-trivial.

5) The Authors focus their model on the 'summer season' (Page 5, Line 3) as this is the period of greatest data density from CVO. Is this dataset also filtered for clear-sky days to reduce comparison bias between the model and measurements? This season is most likely to be affected by cloudy days according to CVO observations reported in (Carpenter et al., 2010). Also, the model compares to HONO measurements from the winter period, when ambient NO_x measurements do not exhibit the same diurnal pattern (i.e. the mid-day maximum) that the majority of this manuscript seeks to explain. It would be useful to present why the authors expect that winter HONO mixing ratios and diurnal structure are representative of summer HONO. Finally, how have the authors included or reasonably excluded boundary layer and transport dynamics in their 0D model? The report from (Carpenter et al., 2010) states that the limited information available in this regard indicates no diel modulation of the boundary layer height, but that it can change substantially from day to day at a site 200 km away. The work cited for DSMACC (Emmerson and Evans, 2009) does not suggest how the boundary layer is represented in the model and it could be that some of the mismatch in early morning and evening NO_x levels is due to mixing and entrainment or local transport phenomena

C3

instead of the model chemistry. It would be useful for the authors to discuss such processes as being accounted for, or as limitations, in the methods and at the appropriate points in the manuscript discussion (e.g. (Wolfe et al., 2016)).

Technical corrections:

Page 1, Line 26: 'the box model simulation' of what? Everything?

Page 2, Line 3: provide a range of typical values for NO_x observations in the remote MBL

Page 2, Lines 13-16: This is an example where the authors specify only particulate nitrate, yet cite work probing a variety of condensed phase nitrate proxies, ranging from surface-adsorbed nitrate to bulk aqueous solutions. The authors should be more specific here regarding the media and interfaces (e.g. particle-gas, surface-gas, aqueous-gas) these works have described and that they have all found an enhancement in nitrate photolysis in the condensed phase although the mechanisms are not well understood.

Page 2, Line 17: Delete 'through'

Page 2, Lines 17-21: Specify that these reactions are all taking place in the gas phase.

Page 3, Line 17: 'for a short period in Nov/Dec 2015' should be restated to the number of days in the winter of 2015, with the observational period explicitly given in the HONO measurement section.

Page 3, Line 23 - Page 4, Line 4: Is assessment of RH and O₃ effects on NO sensitivity and NO₂ converter efficiency at a period of 71 hours assuming that there is little change in sample RH and O₃ over time or that the 1 hour offset in performing this calibration, spread over 2 years, corrects for these diurnal variations over the long term? Also, the measurements reported by (Lee et al., 2009) indicate that this period was 37 hours long. The authors describe in detail how RH of the sample flow is minimized, but do not present information as to the range or relative proportion of RH that sample flows

C4

are reduced to/by. O₃ has a clear diurnal cycle presented throughout the manuscript, so it would be expected that corrections are necessary on an hourly timescale, not once every three days. While many other interferences are clearly detailed for the approach to correction in (Lee et al., 2009; Reed et al., 2016a, 2016b) this particular modification and approach could be more clearly demonstrated to have little variation, with an example of the variability that would be required to have significant systematic bias in the measurement due to RH and O₃ changes within a 71 hour period.

Also, the authors do not present any information about whether aerosols are removed from the sample flow, which could lead to artifact NO_x signals in the system, similarly to other adsorbed species in the photolysis cell. A greater description of the main lab manifold at the beginning of this section would be sufficient to clarify.

Page 4, Line 15: Should 'period' be 'range'? 'being' should be 'are' and since much of this section is reporting data to two significant digits, shouldn't the detection limit for NO of 0.3 be 0.30?

Page 4, Line 21: The 'main lab manifold' is not described above. It would be very useful to have this presented above to know how external air is being delivered to the NO_x instrumentation.

Page 4, Lines 25-26: Do the PM measurements at the site ever indicate the presence of nitrite? Given the prevalence of dust impacting the site, nitrite could be formed on these surfaces. The LOPAP has been shown to effectively sample large aerosols, such as fog droplets, and the authors state dust and sea salt as dominating the mass transport of condensed nitrate to CVO. This could bias the HONO measurement as LOPAP instrumentation does not typically exclude such coarse particles (e.g. (Sörgel et al., 2011)) and the dual-channel scrubbing coils used to quantify background and interference signals only effectively transmit particles less than 1 micrometer in diameter.

Page 6, Line 6: should this sentence finish 'in the instrument inlet'? From (Reed et al., 2016a, 2016b) the thermal decomposition of PAN seems to occur in the photolysis

C5

cell?

Page 6, Lines 10-11: This sentence is describing nocturnal processes, yet photolysis and OH losses are listed. Please correct this error. Also, there is evidence in the presented data that the HONO buildup at night is still occurring (data below 0 pptV at 18:00, and above at 06:00) as would be expected, from the measured precursor NO₂ being present at night and able to undergo heterogeneous hydrolysis. This may not be statistically significant, depending on the uncertainty in the HONO measurement, or the data may only be an estimate based on the exact instrument detection limits, so some clarification here should be given by considering those two limits. Previous work has also shown a rapid approach to steady state in nocturnal HONO in marine environments due to reversible thermodynamic partitioning in marine boundary layer surface waters, which is not mentioned here (Wojtal et al., 2011).

Page 6, Line 17: 'daytime' should be placed between 'additional' and 'source'

Page 6, Lines 19-20: 'are difficult to explain' should be 'cannot be explained'

Page 6, Line 21: 'either of NO_x or HONO'. Shouldn't this be 'NO_x and HONO'?

Page 7, Lines 22-23: The authors should replace 'would appear' with 'is'. Also, it would seem that the intrusion of ship emissions, if stochastic, would be normalized from the mean through the consideration of 2 years of summer data. This is supported by the range versus the mean of the NO_x data presented in many figures.

Page 8, Lines 14-17: It would be expected that the aerosol nitrate would be distributed across both fine and coarse mode aerosol and photolyze differently based on their optical and chemical properties. The authors state in lines 26-28 that this is the case. It would be useful to clarify that the best match of nitrate photolysis enhancement that reproduces observed HONO is a rate integrated across all surface nitrate photolysis sources at CVO since only bulk aerosol composition has been measured in (Fomba et al., 2014).

C6

Page 8, Lines 26-28: It is confusing why the authors cite the (Laufs and Kleffmann, 2016) work here as they state in the abstract of their work, a conclusion counter to the thesis of this work:

'If these results can be translated to atmospheric surfaces, HNO₃ photolysis cannot explain the significant HONO levels in the daytime atmosphere. In addition, it is demonstrated that even the small measured yields of HONO did not result from the direct photolysis of HNO₃ but rather from the consecutive heterogeneous conversion of the primary photolysis product NO₂ on the humid surfaces. The secondary NO₂ conversion was not photoenhanced on pure quartz glass surfaces in good agreement with former studies. A photolysis frequency for the primary reaction product NO₂ of $J(\text{HNO}_3 - \text{NO}_2) = 1.1 \times 10^{-6} \text{ s}^{-1}$ has been calculated (0 SZA, 50% r.h.), which indicates that renoxification by photolysis of adsorbed HNO₃ on non-reactive surfaces is also a minor process in the atmosphere.'

The work described by the cited works of (Baergen and Donaldson, 2013, 2016; Scharko et al., 2014; Ye et al., 2016a, 2016b; Zhou et al., 2003) are all in disagreement with (Laufs and Kleffmann, 2016) and the photolysis rates from these measurements are used to constrain this model. They also clearly discuss the wide range of photolysis values without such contradictory statements. The authors should consider revising the works cited in this location.

Page 9, Line 1: Figure 5 includes PAN transport. Remove the reference to it here.

Page 9, Lines 5-8: The ability to reproduce the NO_x profile is based on a large loss of NO₂ and production of NO, the former of which is not observationally consistent. Stating this and the need to explore further chemical mechanistic constraints would improve the transition to the next section of the manuscript.

Page 9, Line 9: It would be useful to include some reference to halogen chemistry in this section header

C7

Page 9, Line 12: '(NIT)' this is the only instance of this shorthand in the manuscript. Delete.

Page 9, Lines 13-15: This would be much easier to follow if broken into 2-3 sentences.

Page 10, Lines 5-6: Dust and sea salt are stated to be the 'predominant aerosol' at CVO. Is this by number, mass, or surface area? Please specify, with reference to (Carpenter et al., 2010; Fomba et al., 2014), so there is greater clarity in understanding if the majority of the nitrate is expected to be in the coarse mode.

Page 10, Line 14: Delete 'e.g. JPL' and change the citation format to 'Burkholder et al., (2015)'

Page 10, Lines 15-16: It would seem that the heterogeneous chemistry on fine mode aerosol may be what is poorly constrained. Would it be possible to speculate on this?

Page 10, Line 19: 'NO₃' should be 'HNO₃'. Also, is the static reactive uptake coefficient of 0.15 used in the model for HNO₃ partitioning reasonable given the likely need for this value to increase mid-day to sustain the reservoir of particulate nitrate?

Page 12, Lines 8-9: This seems like a transition to an 'Atmospheric Implications' section

Page 12, Line 18: Update this to include the role of other surfaces.

References: Chemical subscripts and capitalization issues need to be corrected in: Burkholder et al (2015), Evans and Jacob (2005), Handley et al (2007), Laufs and Kleffmann (2016), Li et al (2014), Moxim et al (1996), Nakamura et al (2003), Pollack et al (2011), Ryerson et al (2000), Saiz-Lopez et al (2008), Sander et al (1999), Scharko et al (2014), Ye et al (2016a), and Zhou et al (2003)

Figure 1: Why is the NO_x axis red, when the NO_x trace is black? The color scheme here is generally not suitable for red-green color blind individuals and also does not print well in grayscale. Consider a scheme for figures, to use throughout, that is more

C8

easily discerned.

Standard error is weighted by the number of samples considered, but those values are not presented anywhere. It would be worthwhile to do so, especially for the summer period.

The rest of the manuscript only considers the summer observations. Thus, only 'summer' requires a definition of the months considered. Labels in the figure could just be the months considered and would remove the need to cross-reference.

Figure 2: Add the cumulative accuracy and precision error and depict the instrument detection limit.

Figure 3: (left) For all plots like this, would it be more informative to present the values of the difference between the model and the measurement? The color and formatting challenges noted in Figure 1 apply here too. (right) The reaction text is difficult to read and the scale breaks are confusing. Would a log scale work and still emphasize the necessary rates?

Figure 4: This figure could be simplified if the difference between NO_x, NO₂, and NO relative to the observations were depicted in three separate panels for the photolysis factors considered. It would also be a more quantitative representation of which factor is most suitable.

Figure 6: Can the magnitude of the particulate nitrate photolysis be presented here? It would be nice to compare it to the other NO_x source mechanisms. Also, it is surprising that HONO photolysis isn't presented as the manuscript suggests that its intermediate nature is key in reNO_xification at CVO. (right) Same comments as Fig 3. (caption) Insert 'for NO_x' after 'loss analysis'

Figure 7: There is no PAN on this figure, but it is listed in the caption. The difference notation, again, may be more informative for presenting the comparisons.

Figure 8: Could the dips in the early morning NO_x in the model be mismatching the

C9

observations because of NO_x transport or dilution that isn't accounted for in the 0D model?

Figure 11: What do the dashed lines represent?

References

Baergen, A. M. and Donaldson, D. J.: Photochemical renoxification of nitric acid on real urban grime, *Environ. Sci. Technol.*, 47(2), 815–820, doi:10.1021/es3037862, 2013.

Baergen, A. M. and Donaldson, D. J.: Formation of reactive nitrogen oxides from urban grime photochemistry, *Atmos. Chem. Phys.*, 16(10), 6355–6363, doi:10.5194/acp-16-6355-2016, 2016.

Carpenter, L. J., Fleming, Z. L., Read, K. A., Lee, J. D., Moller, S. J., Hopkins, J. R., Purvis, R. M., Lewis, A. C., Müller, K., Heinold, B., Herrmann, H., Fomba, K. W., Van Pinxteren, D., Müller, C., Tegen, I., Wiedensohler, A., Müller, T., Niedermeier, N., Achterberg, E. P., Patey, M. D., Kozlova, E. A., Heimann, M., Heard, D. E., Plane, J. M. C., Mahajan, A., Oetjen, H., Ingham, T., Stone, D., Whalley, L. K., Evans, M. J., Pilling, M. J., Leigh, R. J., Monks, P. S., Karunaharan, A., Vaughan, S., Arnold, S. R., Tschritter, J., Pöhler, D., Frieß, U., Holla, R., Mendes, L. M., Lopez, H., Faria, B., Manning, A. J. and Wallace, D. W. R.: Seasonal characteristics of tropical marine boundary layer air measured at the cape verde atmospheric observatory, *J. Atmos. Chem.*, 67(2–3), 87–140, doi:10.1007/s10874-011-9206-1, 2010.

Cohan, A., Chang, W., Carreras-Sospedra, M. and Dabdub, D.: Influence of sea-salt activated chlorine and surface-mediated renoxification on the weekend effect in the South Coast Air Basin of California, *Atmos. Environ.*, 42(13), 3115–3129, doi:10.1016/j.atmosenv.2007.11.046, 2008.

Crilley, L. R., Kramer, L., Pope, F. D., Whalley, L. K., Cryer, D. R., Heard, D. E., Lee, J. D., Reed, C. and Bloss, W. J.: On the interpretation of in situ HONO observations via photochemical steady state, *Faraday Discuss.*, 189(0), 191–212,

C10

doi:10.1039/C5FD00224A, 2016.

Emmerson, K. M. and Evans, M. J.: Comparison of tropospheric gas-phase chemistry schemes for use within global models, *Atmos. Chem. Phys.*, (1990), 1831–1845, doi:10.5194/acpd-8-19957-2008, 2009.

Fomba, K. W., Müller, K., Van Pinxteren, D., Poulain, L., Van Pinxteren, M. and Herrmann, H.: Long-term chemical characterization of tropical and marine aerosols at the Cape Verde Atmospheric Observatory (CVAO) from 2007 to 2011, *Atmos. Chem. Phys.*, 14(17), 8883–8904, doi:10.5194/acp-14-8883-2014, 2014.

Handley, S. R., Clifford, D. and Donaldson, D. J.: Photochemical loss of nitric acid on organic films: A possible recycling mechanism for NO_x, *Environ. Sci. Technol.*, 41(11), 3898–3903, doi:10.1021/es062044z, 2007.

Heland, J., Kleffmann, J., Kurtenbach, R. and Wiesen, P.: A new instrument to measure gaseous nitrous acid (HONO) in the atmosphere, *Environ. Sci. Technol.*, 35(15), 3207–3212, doi:10.1021/es000303t, 2001. Laufs, S. and Kleffmann, J.: Investigations on HONO formation from photolysis of adsorbed HNO₃ on quartz glass surfaces, *Phys. Chem. Chem. Phys.*, 18(14), 9616–9625, doi:10.1039/c6cp00436a, 2016.

Lee, J. D., Moller, S. J., Read, K. A., Lewis, A. C., Mendes, L. and Carpenter, L. J.: Year-round measurements of nitrogen oxides and ozone in the tropical North Atlantic marine boundary layer, *J. Geophys. Res. Atmos.*, 114(21), 1–14, doi:10.1029/2009JD011878, 2009.

Ndour, M., Conchon, P., D'Anna, B., Ka, O. and George, C.: Photochemistry of mineral dust surface as a potential atmospheric renoxification process, *Geophys. Res. Lett.*, 36(5), 2–5, doi:10.1029/2008GL036662, 2009.

Reed, C., Brumby, C. A., Crilley, L. R., Kramer, L. J., Bloss, W. J., Seakins, P. W., Lee, J. D. and Carpenter, L. J.: HONO Measurement by Differential Photolysis, *Atmos. Meas. Tech. Discuss.*, (2), 1–28, doi:10.5194/amt-2016-17, 2016a.

C11

Reed, C., Evans, M. J., Di Carlo, P., Lee, J. D. and Carpenter, L. J.: Interferences in photolytic NO₂ measurements: Explanation for an apparent missing oxidant?, *Atmos. Chem. Phys.*, 16(7), 4707–4724, doi:10.5194/acp-16-4707-2016, 2016b.

Scharko, N. K., Berke, A. E. and Raff, J. D.: Release of Nitrous Acid and Nitrogen Dioxide from Nitrate Photolysis in Acidic Aqueous Solutions, *Environ. Sci. Technol.*, doi:10.1021/es503088x, 2014.

Sörgel, M., Trebs, I., Serafimovich, A., Moravek, A., Held, A. and Zetzsch, C.: Simultaneous HONO measurements in and above a forest canopy: Influence of turbulent exchange on mixing ratio differences, *Atmos. Chem. Phys.*, 11(2), 841–855, doi:10.5194/acp-11-841-2011, 2011.

Wojtal, P., Halla, J. D. and McLaren, R.: Pseudo steady states of HONO measured in the nocturnal marine boundary layer: A conceptual model for HONO formation on aqueous surfaces, *Atmos. Chem. Phys.*, 11(7), 3243–3261, doi:10.5194/acp-11-3243-2011, 2011. Wolfe, G. M., Marvin, M. R., Roberts, S. J., Travis, K. R. and Liao, J.: The framework for 0-D atmospheric modeling (FOAM) v3.1, *Geosci. Model Dev.*, 9(9), 3309–3319, doi:10.5194/gmd-9-3309-2016, 2016.

Ye, C., Gao, H., Zhang, N. and Zhou, X.: Photolysis of Nitric Acid and Nitrate on Natural and Artificial Surfaces, *Environ. Sci. Technol.*, 50(7), 3530–3536, doi:10.1021/acs.est.5b05032, 2016a.

Ye, C., Zhou, X., Pu, D., Stutz, J., Festa, J., Spolaor, M., Tsai, C., Cantrell, C., Mauldin, R. L., Campos, T., Weinheimer, A., Hornbrook, R. S., Apel, E. C., Guenther, A., Kaser, L., Yuan, B., Karl, T., Haggerty, J., Hall, S., Ullmann, K., Smith, J. N., Ortega, J. and Knote, C.: Rapid cycling of reactive nitrogen in the marine boundary layer., *Nature*, 532(7600), doi:10.1038/nature17195, 2016b.

Zhou, X., Gao, H., He, Y., Huang, G., Bertman, S. B., Civerolo, K. and Schwab, J.: Nitric acid photolysis on surfaces in low-NO_x environments: Significant atmospheric

C12

implications, *Geophys. Res. Lett.*, 30(23), 2217, doi:10.1029/2003GL018620, 2003.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2016-1111, 2017.